TITLE:

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AUTHOR(S):

Katagiri, Takao

CITATION:

Katagiri, Takao. Reaction between Acetylene and Propylene. (I) : Reaction Products by Catalytic Pyrolysis under Atmospheric Pressure. Bulletin of the Institute for Chemical Research, Kyoto University 1963, 41(2-4): 159-169

ISSUE DATE:

1963-10-10

URL:

http://hdl.handle.net/2433/75972

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Reaction between Acetylene and Propylene. (I)

Reaction Products by Catalytic Pyrolysis under Atmospheric Pressure

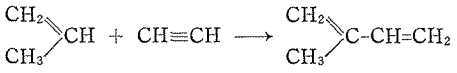
Takao KATAGIRI*

(Kunichika Laboratory)

Received March 30, 1963

There are many reports on the vapor phase catalytic pyrolysis of the mixture of acetylene and propylene for the preparation of isoprene, but the mechanism of the reaction is not yet clear. As a synthetic method of isoprene, the author has been interested in this reaction and studied it with unsuccessful results. Therefore, he has tried to find the reason why isoprene is not produced with good yields in the reaction under atmospheric pressure. In the present paper, the results of the analysis of the products in the pyrolysis with various catalysts are reported. The main products were lower hydrocarbons and hydrogen. When copper chlorides were used as the catalysts, methyl chloride was found in the products.

In the end of the last century, Berthelot[1] studied the reaction of propylene with acetylene at 500° using copper tube and reported that isoprene was produced in a high yield.



After this, several German patents on this reaction appeared in the literature. There are also many reports such as those with silicic and titanic acids as catalysts[2], with oxides or hydroxides of alkali metals under pressure[3], etc. Recently in U.S.S.R., Nazarov and his coworkers[4] reported on this reaction with metal oxides as the catalysts. Despite that this reaction has been studied for so long a time, it appears that the preparation of isoprene by this reaction has been given up without getting detailed knowledge on it.

The author has studied this gas reaction with various catalyst to determine the reaction mechanism. The reaction has been investigated at 250°-430° under atmospheric pressure with catalysts such as metals or their salts.

The products were analyzed mostly by gas chromatographic method and in some cases by infrared spectroscopic method. The results are shown in Tables 1-6.

Data showed that the products contained small amounts of compounds having isoprene skeleton and relatively large amounts of the other substances such as hydrogen, methane, ethane, ethylene, and propane.

From these results, it is clear that Berthelot's results mentioned above must be reexamined.

* 片 桐 孝 夫

Table 1. Reaction products by the activated alumina catalyst.

Reaction temperature (°C)		250	300	350	400	430
Conversion (Vol. %)	acetylene	35.0	35.0	40.8	48.0	50.5
	propylene	12.8	12.6	19.6	28.5	32.3
Products (Vol. %)	hydrogen	26.0	25.3	24.1	23.4	22.4
	methane	2.3	2.9	5.7	7.8	10.5
	ethane	0	5.6	11.3	14.3	15.7
	ethylene	0	3.8	7.5	5.2	4.5
	propane	6.4	6.8	7.4	9.1	12.2
	1-butene	6.7	7.7	15.8	12.0	6.8
	2-butene	3.2	6.4	5.6	3.8	2.3
	1,3-butadiene	4.6	3.7	2.1	0.3	0.2
	1-pentene	26.9	11.8	4.7	6.8	6.0
	2-methyl butane	4.2	9.3	3.7	5.0	3.0
	2-methyl-1-butene	12.4	7.1	2.1	1.9	2.2
	3-methyl-1-butene	0	0	0	0	0.2
	isoprene	1.0	1.6	2.2	1.8	1.5
	hexenes	3.0	4.7	5.4	6.1	9.9
	2-methyl pentane	2.2	2.3	2.3	2.7	2.6
	4-methyl-1-pentene	1.3	0.9	0.2	0	0
Volume change (%)		19.7	27.8	41.7	64.6	82.0

Table 2. Reaction products by the copper-alumina catalyst.

Reaction temperature (°C)		250	300	350	400	430
Conversion (Vol. %)	acetylene	96	98	99	100	100
	propylene	68	79	85	90	91
Products (Vol. %)	hydrogen	25.3	22.8	17.5	13.2	9.0
	methane	2.9	9.6	16.5	23.0	27.3
	ethane	10.9	16.2	23.8	13.4	10.3
	ethylene	4.3	5.0	7.7	9.8	11.9
	propane	6.2	8.7	12.7	17.0	20.4
	1-butene	2.5	2.7	4.9	7.4	11.0
	2-butene	0.3	0.4	1.1	1.9	1.9
	1,3-butadiene	3.9	2.8	0.8	0.9	0.2
	1-pentene	14.8	11.0	4.6	4.6	2.3
	2-pentene	0.8	0.9	0.8	0.7	0.8
	1,4-pentadiene	6.2	3.7	1.3	0.6	0.1
	2-methyl butane	0.4	0.8	1.7	2.4	2.7
	2-methyl-1-butene	9.5	7.2	2.0	1.8	0.4
	isoprene	3.2	2.3	1.0	0.8	0.2
	hexenes	7.6	4.7	2.7	1.4	1.3
	2,3-dimethyl-1-butene	1.2	1.2	1.0	1.1	0.5
Volume change (%)		4.0	11.2	20.1	25.7	30.8

Table 3. Reaction products by the cuprous chloride-alumina catalyst.

Reaction temperature (°C)		250	300	350	400	430
Conversion (Vol. %)	acetylene	85.1	96.3	98.7	99.5	100
	propylene	61.0	74.2	78.5	85.3	88.9
Products (Vol. %)	hydrogen	5.8	11.8	22.3	20.5	19.1
	methane	0	0	9.0	14.5	18.3
	methyl chloride	13.4	5.2	2.1	2.2	1.5
	ethane	0	10.4	20.9	25.0	27.7
	ethylene	8.5	20.5	18.3	18.0	15.6
	propane	48.2	26.3	15.7	11.5	9.3
	1-butene	0	3.2	2.7	2.9	3.0
	2-butene	0	1.2	0.9	0.9	0.8
	1,3-butadiene	0	2.3	0.4	0.4	0.1
	1-pentene	4.8	3.3	0	0	0
	2-methyl butane	0	1.0	1.0	1.2	1.5
	2-methyl-1-butene	0	4.1	1.0	1.2	0.4
	3-methyl-1-butene	7.3	6.2	3.2	0	0
	hexenes	12.0	3.9	2.3	1.7	2.4
	4-methyl-1-pentene	0	0.6	0.2	0.4	0.3
Volume change (%)		−3.1	5.5	28.0	36.8	44.6

Table 4. Reaction products by the cupric chloride-alumina catalyst.

Reaction temperature (°C)		250	300	350	400	430
Conversion (Vol. %)	acetylene	98.0	99.0	99.5	100	100
	propylene	58.0	60.5	63.5	72.0	84.0
Products (Vol. %)	hydrogen	7.8	11.0	22.8	21.2	16.9
	methane	0	0	2.6	12.8	14.5
	methyl chloride	9.6	14.0	10.9	3.5	0.9
	ethane	2.6	2.7	15.0	24.6	24.3
	ethylene	22.0	11.1	8.1	7.7	8.0
	propane	27.4	27.0	13.5	9.1	8.4
	1-butene	10.5	9.5	7.6	6.5	6.0
	2-butene	0.5	0.9	1.0	1.2	2.1
	1,3-butadiene	1.4	1.1	0.8	0.3	0.4
	1-pentene	4.7	8.9	5.4	3.0	2.4
	2-pentene	5.6	5.6	5.1	4.0	2.4
	2-methyl butane	1.6	2.8	3.1	2.9	3.1
	2-methyl-1-butene	0	0	0	1.1	3.0
	3-methyl-1-butene	2.6	3.1	2.9	1.2	2.4
	isoprene	3.7	2.1	1.2	0.6	0.4
	hexenes	0	0	0	0	4.3
	4-methyl-1-pentene	0	0	0	0.2	0.6
Volume change (%)		−1.7	6.9	20.8	36.1	40.3

Table 5. Reaction products by the nickel oxide-alumina catalyst.

Reaction temperature (°C)		250	300	350	400	430
Conversion (Vol. %)	acetylene		95.0	98.0	100	100
	propylene		21.3	25.7	38.4	48.5
Products (Vol.%)	hydrogen	No reaction occurred	26.1	24.6	23.1	22.0
	methane		4.9	3.2	2.7	2.4
	ethane		5.4	4.8	5.4	7.0
	ethylene		19.4	12.3	8.5	3.2
	propane		30.2	37.2	39.5	45.2
	1-butene		3.7	7.8	7.8	8.8
	2-butene		1.7	2.1	2.3	2.1
	1,3-butadiene		2.6	1.2	0.8	0.6
	1-pentene		1.7	1.8	3.7	2.7
	2-methyl butane		1.6	2.9	2.9	1.6
	2-methyl-1-butene		1.5	0.7	0.5	0.2
	isoprene		0	0.4	0.5	0.5
	2-methyl-1-pentene		0.3	0.6	1.9	3.1
	4-methyl-1-pentene		0.9	0.7	0.5	0.3
	2,3-dimetyyl-1-butene		0	0	0	0.2
Volume change (%)			23.0	36.6	50.8	65.6

Table 6. Reaction products by the silver-alumina catalyst.

Reaction temperature (°C)		250	300	350	400	430
Conversion (Vol. %)	acetylene	90.5	96.5	98.5	99.5	100
	propylene	64.5	69.0	76.5	86.5	92.5
Products (Vol. %)	hydrogen	39.1	35.4	32.1	26.6	21.7
	methane	22.5	21.8	21.4	21.7	21.4
	ethane	7.5	7.5	9.9	11.3	12.3
	ethylene	15.2	15.4	14.9	13.7	13.1
	propane	7.9	9.0	11.6	15.9	19.6
	1-butene	0.3	0.9	1.3	1.4	2.7
	2-butene	0.4	0.7	0.9	1.0	1.3
	1,3-butadiene	1.8	1.2	0.9	0.6	0.3
	1-pentene	0.5	1.0	1.4	2.2	3.0
	2-pentene	0	0.2	0.2	0.5	0.7
	1,4-pentadiene	0	0	0.1	0.3	0.4
	2-methyl butane	0.3	0.6	1.2	1.7	1.8
	2-methyl-1-butene	1.2	3.2	2.0	1.6	1.3
	3-methyl-1-butene	0	0.4	0.3	0.2	0.1
	isoprene	0	0	0.1	0.1	0.1
	hexenes	3.4	2.4	1.6	0.9	0.3
	3-methyl pentane	0	0	0	0	0.2
Volume change (%)		29.6	35.3	47.8	67.7	89.2

EXPERIMENTAL

1) Materials

Acetylene was obtained from a commercial cylinder and purified by washing with saturated aqueous solution of sodium bisulfite and then with water. Purity of the acetylene was 99.0% (analyzed by gas chromatographic method).

Propylene was prepared by the dehydration of isopropanol with activated alumina at 400° and washed with 10% sodium hydroxide solution to remove carbon dioxide. Purity of the propylene was 99.0%.

2) Catalysts

Activated alumina. Activated alumina tablets for drying were used without further treating.

Copper-alumina. Purified cupric chloride (5.4g.) was dissolved in 20ml. of water, and to this solution, 25g. of activated alumina tablets were added. This mixture was evaporated to dryness on a steam bath with stirring. The dried tablets were packed in a reaction tube and reduced with hydrogen at 400° for 5 hours untill no hydrogen chloride could be detected.

Cuprous chloride-alumina. Purified cuprous chloride (3.1g.) was dissolved in 10ml. of 6*N*-hydrochloric acid, and to this solution 25g. of activated alumina tablets were added. This mixture was evaporated to dryness under reduced pressure without heating. Water (100ml.) was added to this residue to decompose the complex salt of cuprous chloride with hydrogen chloride. The tablets were taken out of the mixture and dried on silica gel in vacuo.

Cupric chloride-alumina. This was obtained by the same procedure as described for the preparation of copper-alumina catalyst, except that it was reduced with hydrogen.

Nickel oxide-alumina. Purified nickel nitrate (9.9g.) was dissolved in 30ml. of water, and 25g. of activated alumina tablets were added to this solution. This mixture was evaporated to dryness on a steam bath with stirring. The dried tablets were packed in a reaction tube and oxidized by air at 400° for 5 hours. It was confirmed that no formation of acidic gas was detected during this procedure.

Silver-alumina. In a brown bottle, 3.2g. of silver nitrate was dissolved in 30ml. of water, and 25g. of activated alumina tablets were added to this solution. The mixture was evaporated on a steam bath with stirring. The tablets were packed in a reaction tube and reduced with hydrogen at 400° for 7 hours. No formation of acidic gas was detected during this procedure.

3) Reaction Apparatus and Procedure

The apparatus for the experiments is shown in Fig.1. The gas holder (A) was filled with a mixture of acetylene, propylene and nitrogen. Nitrogen was used for the convenience to determine the increase of the volume by the reaction. Mixing ratio was 45:45:10. The pressure of the mixed gas (150mm. water) was controlled by a manometer (B) and a Mariotte's bottle (M). The mixed gas was dried with silica gel (D), and led to the reaction tube. The reaction tube (R)

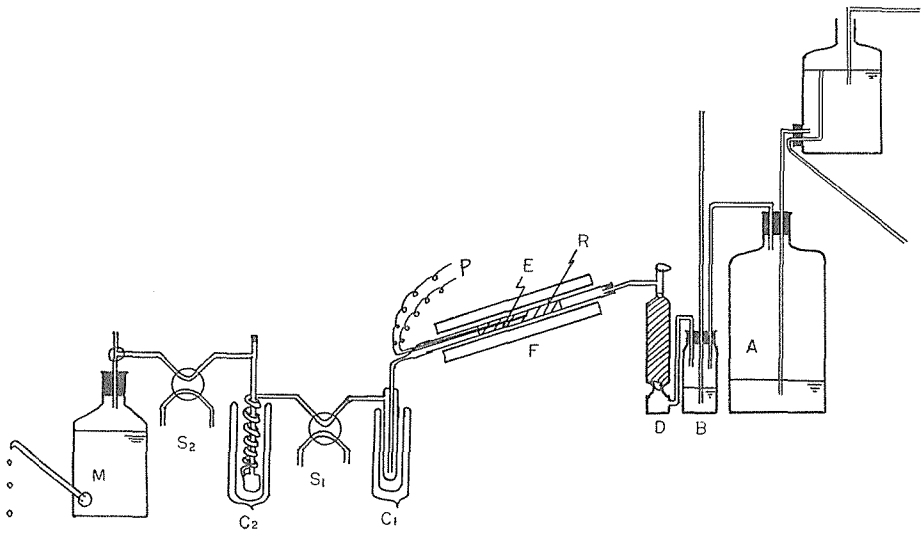


Fig. 1. Reaction apparatus.

A, gas holder; B, manometer; C's, traps; D, drying tower packed with silica gel; E, catalyst; F, electric furnace; M, Mariotte's bottle; P, pyrometer; R, reaction tube; S's. sampling cocks.

was packed with 25ml. of a catalyst (E), and a thermo-couple (P) was inserted into the catalyst bed to measure the reaction temperature. The reacted gas was led to a ice cooled trap (C_1), and to the first sampling cook (S_1). The sample was collected through this cock and analyzed. The gas was then led to a trap which was cooled to $-35°$ with methanol and dry-ice (C_2). In this trap, substances having boiling points higher than $-30°$ were liquified, and those gases having boiling points lower than that of propylene were collected through the second sampling cock (S_2). The reaction temperature was controlled by an electric furnace (F).

The reaction tube packed with catalyst was placed in the furnace, the air in it was replaced with nitrogen, and the temperature was elevated to 250°. The feed gas was then introduced to the reaction tube at a flow rate of 100ml./min. (SV=240l./hr./l.). After thirty minutes, samples were collected through the first and second sampling cocks. The temperature was then elevated to a higher one and kept for half an hour with the same flow of the feed gas, and the samples at this temperature were collected. This procedures were repeated until the reaction temperature became 430°.

4) Analysis

Reaction products were analyzed mostly by gas chromatographic method, and in some cases identified by infrared spectroscopic method.

Gas chromatographic method. The samples taken from the first sampling cock were analyzed at 25° by three kinds of 2m.-columns which were packed with 2,4-dimethyl sulforane, β,β'-dioxypropionitrile, and dioctyl phthalate supported on fire brick C-22 (60-80 mesh), respectively (10% liquids on the supporter).

Table 7. Relative retention times of methyl chloride and some hydrocarbons. (25°)

	stationary phase		
	2,4-Dimethyl sulforane	β,β′-Dioxy propionitrile	Dioctyl phthalate*
Propylene	0.023	0.014	0.051
2-Methyl butane	0.075	0.021	0.399
1-Pentene	0.155	0.055	0.53
Methyl chloride	0.167	0.052	0.739

* According to the author's experiment, Hively's data with dinonyl phthalate could be used for those with dioctyl phthalate.

Table 8. Relative retention times of hydrogen, nitrogen, and some lower hydrocarbons. (25ml./min. H_2 or N_2: Temp. 60°)

Fixed phase	2,4-dimethyl sulforane 10 wt.%/silica gel		β,β′-dioxypropionitrile 10wt.%/silica gel
Gas phase	H_2	N_2	H_2
Hydrogen	—	0.0578	—
Nitrogen	0.0505	—	0.092
Methane	0.076	0.0867	0.104
Ethane	0.0268	0.156	0.250
Ethylene	0.414	0.294	0.318
Propane	0.825	0.651	0.609
Acetylene	0.742	0.659	0.680
Propylene*	1.000	1.000	1.000

* Propylene is used as the standard substance.

This analysis was carried out according to Hively's experiments[5], and his data were checked by some authentic substances*.

Methyl chloride, which was not included in his data, was studied with the three columns above and the results are shown in Table 7.

The samples from the second cock were analyzed at 60° by two kinds of 2m.-columns, which were packed with 2,4-dimethyl sulforane and β,β′-dioxypropionitrile supported on silica gel (80-100 mesh), respectively (10% liquids on the supporter). The relative retention times of the authentic samples with the two columns above are shown in Table 8.

Infrared spectrescopic method. Among the substances separated with the gas chromatogaph, methyl chloride, 1-butene, 2-butene, 2-methyl butane, 1-pentene, and isoprene were identified by infrared spectra.

Methyl chloride, 1-butene, and 2-butene were collected as liquids in a dry-ice-methanol trap at −70° respectively from the exit gas of the gas-chromatograph, evaporated and led to gas cell (10cm. length) for spectroscopic analysis. The

* Acetylene, propylene, 1-butene, 1,3-butadiene, 3-methyl-1-butene, 1,4-pentadiene, 2-methyl butane, 1-pentene, 2-methyl-1-butene, and isoprene.

same procedures were applied to 2-methyl butane, 1-pentene, and isoprene. These compounds were trapped at −40°, and IR. spectra were determined. These spectra were identical with those of the authentic samples as shown in Figs.2-7.

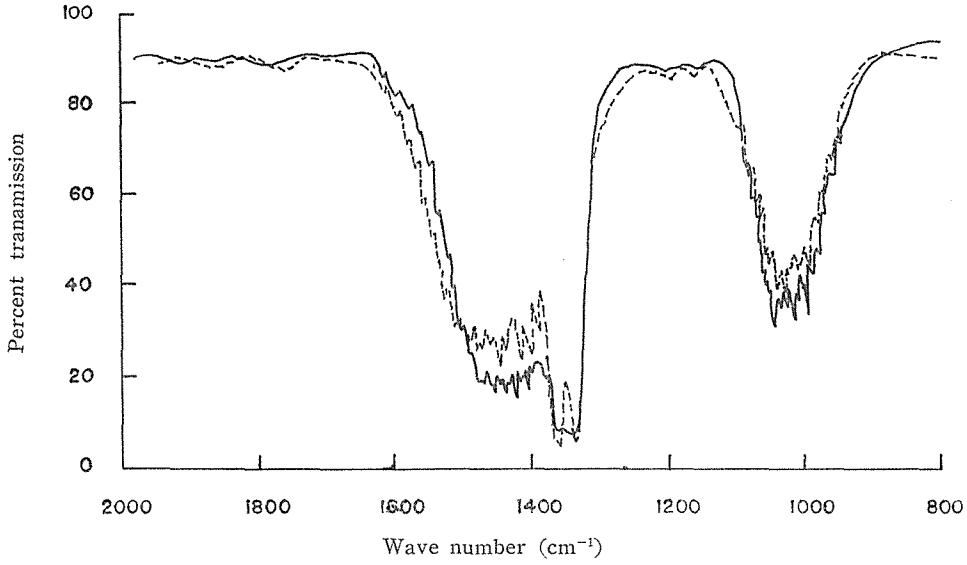


Fig. 2. Infrared absorption spectra of methyl chloride. (solid line is taken from Ref. (6), dotted line is the observed.)

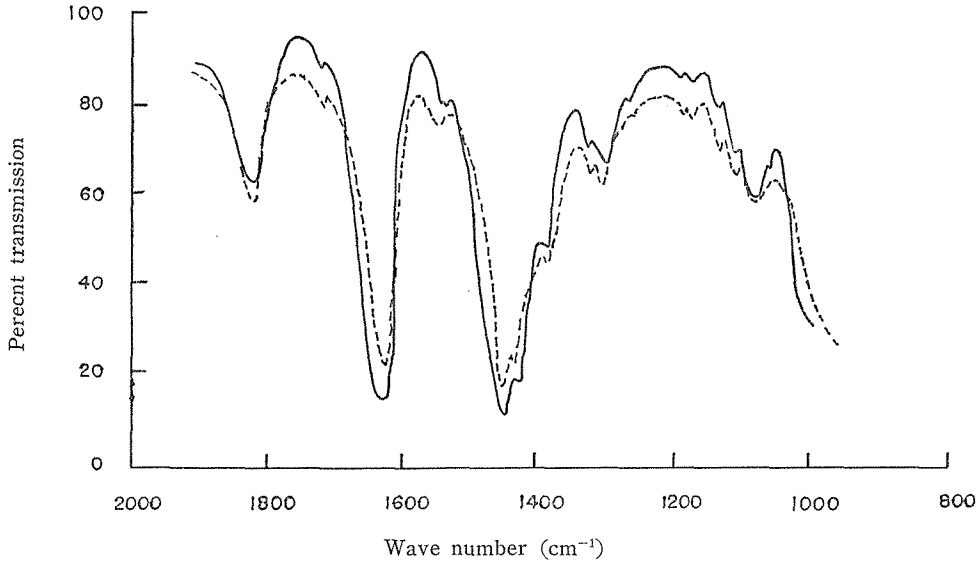


Fig. 3. Infrared absorption spectra of 1-butene. (solid line is taken from Ref.(7), dotted line is the observed.)

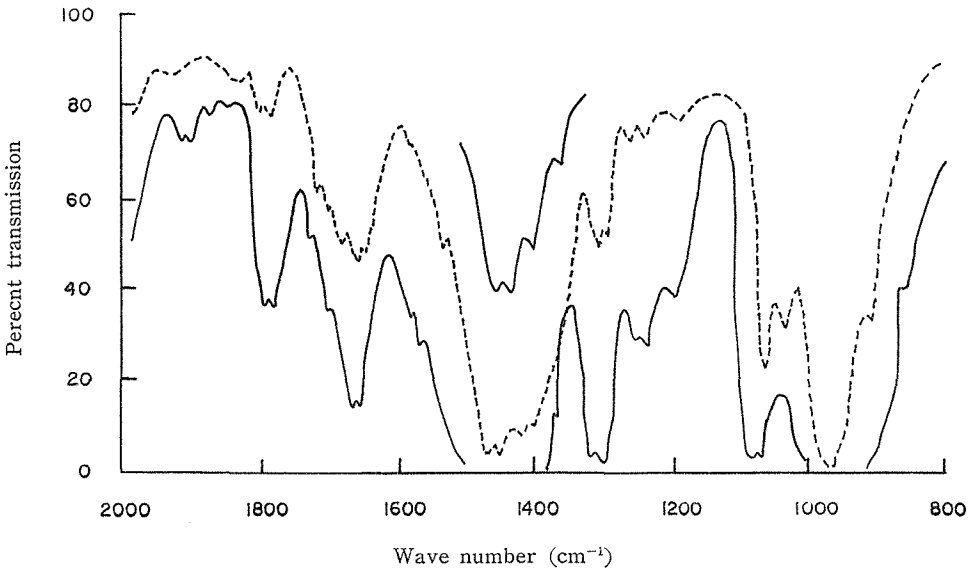


Fig. 4. Infrared absorption spectra of 2-butene. (solid line is taken from Ref. (8), dotted line is the observed.)

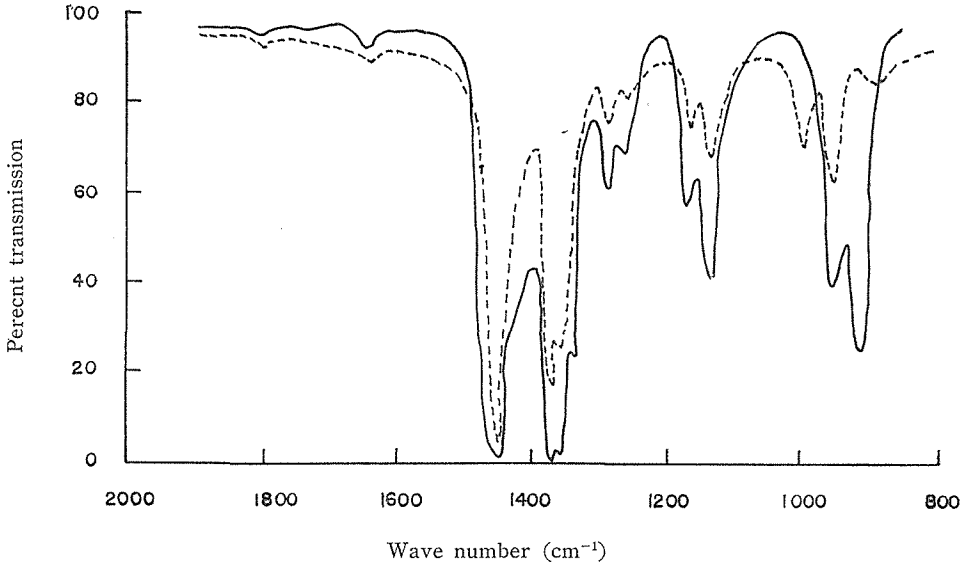


Fig. 5. Infrared absorption spectra of 2-methyl butane. (solid line is taken from Ref. (9), dotted line is the observed.)

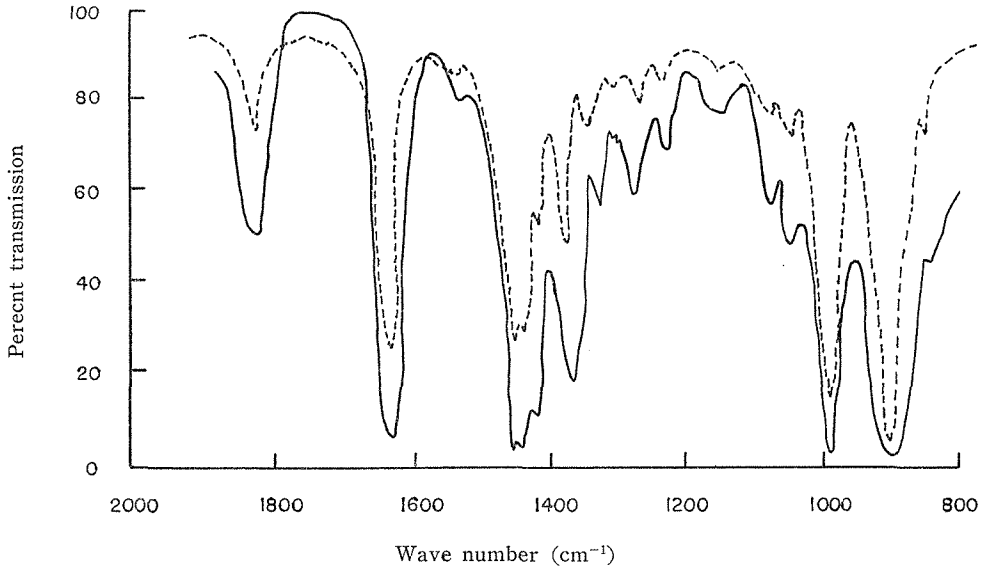


Fig. 6. Infrared absorption spectra of 1-pentene. (solid line is taken from Ref. (10), dotted line is the observed.)

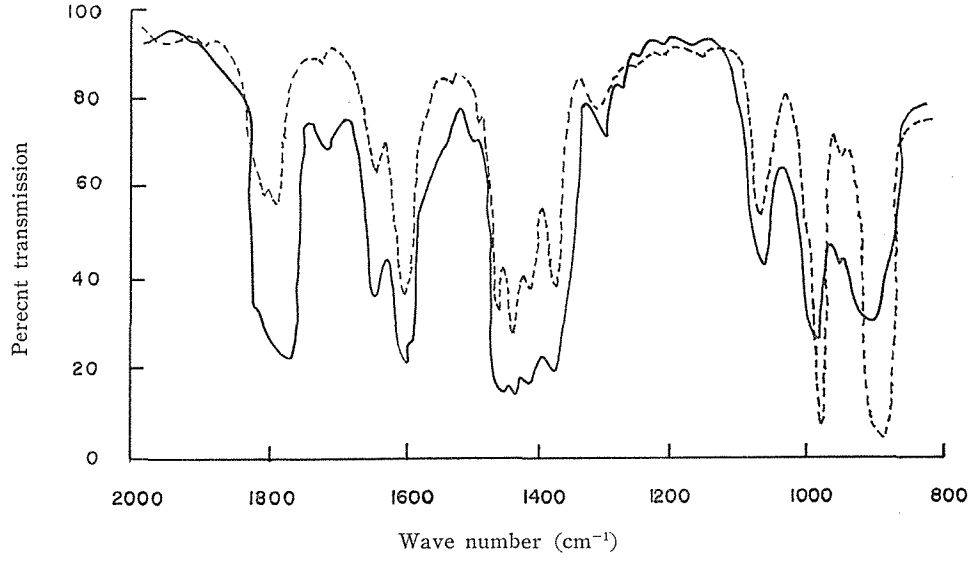


Fig. 7. Infrared absorption spectra of isoprene. (solid line is taken from Ref. (11), dotted line is the observed.)

The author wishes to express his sincere thanks to Professor Sango Kunichika and Professor Ryozo Goto, of Kyoto University, for their kind guidance and encouragement.

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